Global and Regional Impacts of HONO on the Chemical Composition of Clouds and Aerosols

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Introduction

- HONO photolysis is an important source of the OH radical, the primary oxidant of the atmosphere, responsible for the removal of most reactive gases.
- Owing to the incomplete knowledge of HONO sources, realistic HONO mechanisms have not yet been implemented in global models.
- Recently, realistic simulation of HONO based on a HONO/NO_x ratio of 0.02 was found to have a significant impact on the global budgets of HO_x ($OH+HO_2$) and secondary oxidation products, especially in winter (Elshorbany et al., 2012).
- Underestimation of sulphate aerosols has been reported by several studies, especially during winter, which was attributed to missing oxidation pathways.
- Enhanced H_2SO_4 and HNO_3 as a result of realistic HONO simulations may improve aerosol simulations in high NO_x regions.

Aim of the Work

- Investigate the impact of simulating realistic HONO levels on aerosol and cloud compositions under different conditions, both on regional and global scale.

Modelling Approach

ECHAMv5.3.01/MESSy v2.42 Atmospheric Chemistry (EMAC) model (Jöckel et al., 2005, 2006, 2010):

Reference runs (Base_S#):
- Base_S1: Simulation Period: 2000-2001
  Resolution: T42L31MA (about 2.8°×2.8°)
  HONO chemistry: default setup, only HONO pss.
- Base_S2: as Base_S1 except SCAV=EASY, no aqueous phase chemistry.
- Base_S3: as Base_S1 except SO_2+OH=DUMMY, no H_2SO_4 production.

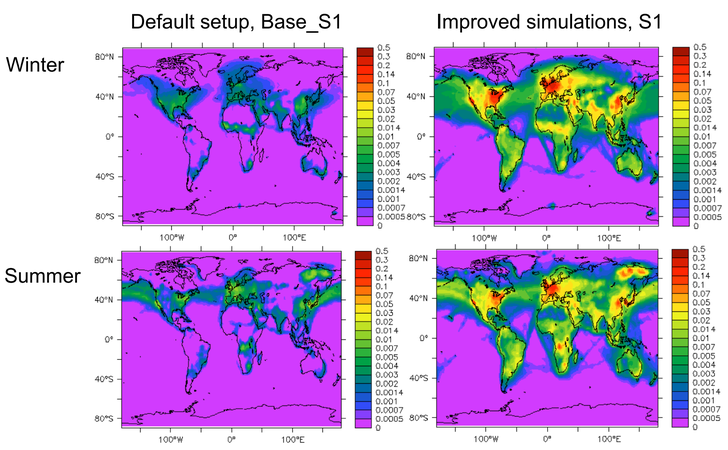
Sensitivity runs (S_#):
- S1: as Base_S1 except HONO: Iterative correction of HONO/NO_x ratio= 0.02 with integration time set to 1 min.
- S2: as S1 except SCAV=EASY, no aqueous phase chemistry.
- S3: as S1 except SO_2+OH=DUMMY, no H_2SO_4 production.

Measurement Networks

The simulated aerosol concentrations are compared with:
CASTNET (54 station): North America
EMEP (81 station): Europe
EANET (10 station): Asia

Results and Discussion

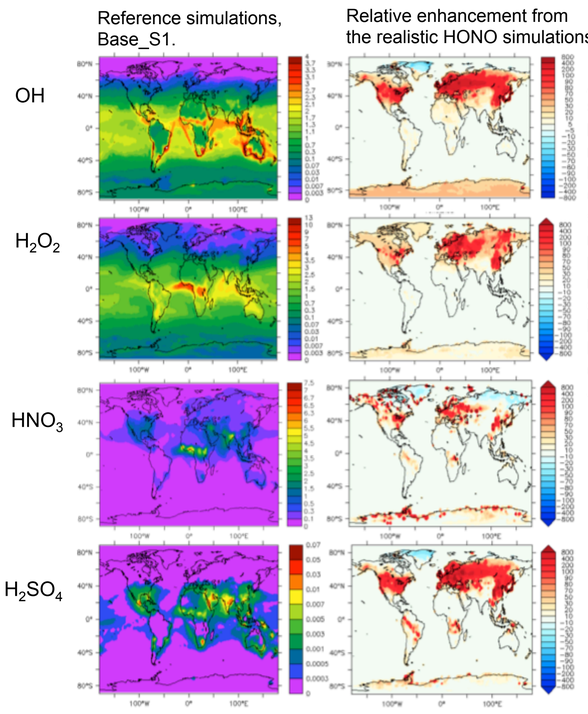
- **Realistic HONO simulations**



Simulated monthly average HONO mixing ratios (ppbv) from the reference run (Base_S1, left) and the sensitivity run (S1, i.e, using a HONO/NO_x ratio of 0.02) near the surface in January (upper panels) and July (lower panels).

➢ Simulated HONO levels are about tenfold higher than the base scenario, which considers the known gas phase formation (OH +NO→HONO) as a sole source of HONO, in agreement with previous measurement-modelling studies (Elshorbany et al., 2012).

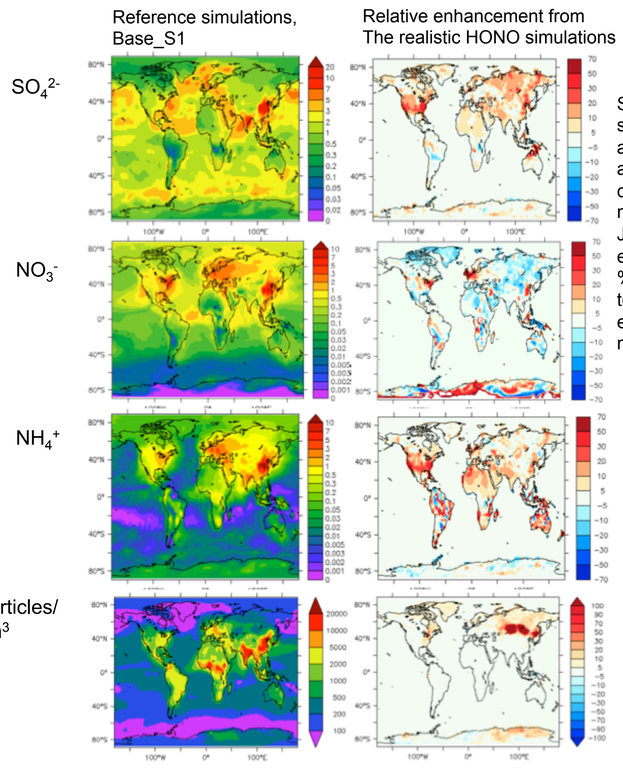
- **HO_x and secondary oxidation products**



Average simulated OH (from top to bottom) (10^6 molecules cm^{-3}), H_2O_2, HNO_3, H_2SO_4 (ppbv) near the surface from the reference run (left panels) and their relative enhancements (%) by using a HONO/NO_x ratio of 0.02 (right panels) in January.

➢ HO_x, H_2O_2, HNO_3, H_2SO_4 are enhanced in high NO_x regions as a result of simulating realistic HONO levels, especially in winter, when other photolytic sources are of minor importance.

- **Aerosol composition**
  - **Global Impact**



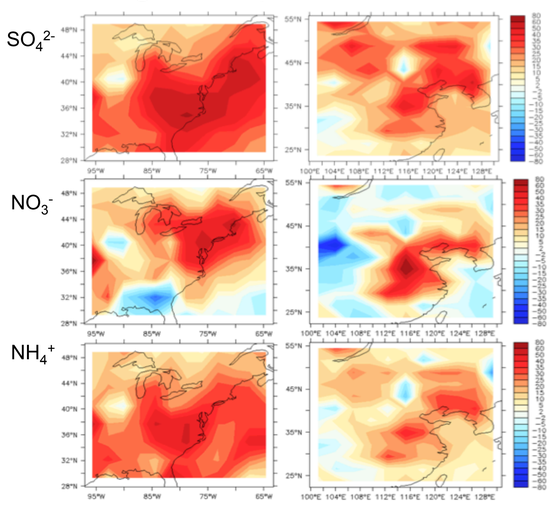
Simulated aerosol sulphate, nitrate and ammonium ($\mu g/m^3$) and number concentration (cm^{-3}) near the surface in January and relative enhancements (in %, right panels) due to HONO enhancement in the model.

➢ Sulphates: Enhanced in high NO_x, high NH_4 regions and mainly due to enhanced OH+SO_2 reaction. **H_2O_2** oxidation of S(IV) did not contributed to enhanced SO_4^{2-} (→ S(IV) limited conditions except in E. Asia).

➢ Nitrates: Enhanced due to:
1. Enhanced HNO_3 in high NO_x, high NH_4 regions.
2. Due to enhanced N_2O_5 hydrolysis on sulphate aerosol particles in high NH_4^+ regions.
   ➢ Enhanced SO_4^{2-} in limited NH_4 regions may decrease NO_3^- levels.

➢ Aerosol number concentrations: Enhanced in high NO_x, high NH_4 regions and mainly due to enhanced H_2SO_4.

  - **Regional Impact**

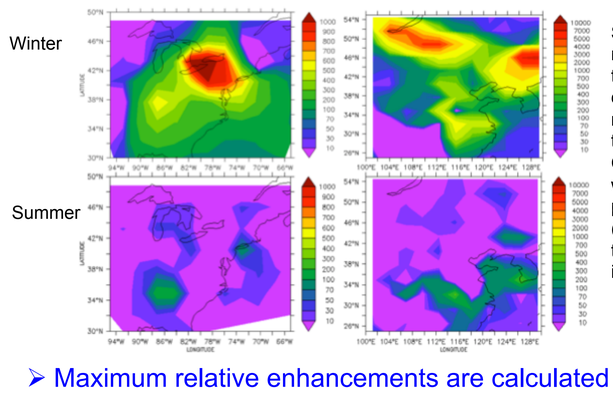


Simulated monthly average relative enhancements (%) in the aerosol (accumulation soluble mode, as) sulphates (upper panels), nitrates (middle panels) and ammonium (lower panels) near the surface in January over the eastern US (left) and China (right).

➢ Sulphates: In eastern US, sulphates are significantly enhanced with **OH**+SO_2→ H_2SO_4 reaction being more important than H_2O_2 oxidation of S(IV) as a result of realistic HONO simulations.

➢ Nitrates: is enhanced in high NO_x, high NH_4^+ regions but are reduced in NH_4^+ limited regions.

- **Aerosol number concentrations**



Simulated monthly mean enhancement in the aerosol number concentrations (cm^{-3}) near the surface over the eastern US (left) and China (right) during winter (January, upper panels) and summer (July, lower panels) due to HONO enhancement in the model.

➢ Maximum relative enhancements are calculated during the winter season with an increase of 10^4 cm^{-3} in eastern China, about one order of magnitude higher than that over the eastern US.

aerosol mode	run	aerosol number concentration			
		eastern US[1]		eastern China[2]	
		cm^{-3}	% *	cm^{-3}	% *
total aerosol	**S1**	**2032**	**10**	**5520**	**11**
	S3	**1956**	**-0.3**	**5438**	**-0.1**
ns	**S1**	8.51	681	10.4	5131
	S3	7.59×10^{-4}	48	1.07×10^{-3}	-37
ks	**S1**	552	44	825	31
	S3	358	2	550	1
as	**S1**	235	27	567	14
	S3	148	1	369	2
cs	**S1**	1.40	0.6	2.61	-2
	S3	1.33	0.2	2.70	-4
ki	**S1**	1235	-13	4075	-6
	S3	1448	-1	4472	-1
ai	**S1**	5.97×10^{-3}	-38	33.9	2
	S3	1.15×10^{-1}	-2	39.1	2
ci	**S1**	1.08×10^{-3}	-30	2.74	2
	S3	5.73×10^{-3}	-1	3.10	1

*) Relative enhancement as a result of simulating realistic HONO levels (S1 run). Abbreviations "ns, ks, as and cs" refer to nucleation, Aitken, accumulation and coarse soluble aerosol modes, respectively, while "ki, ai and ci" refer to the corresponding insoluble modes. Data are averaged over the eastern 1) US (95-65°W, 30-50°N) and 2) China (100-130°E, 25-55°N).

➢ Aerosol number concentrations:
1. Dominated by the ks and as modes (→ typical surface distribution).
2. Mean relative enhancement over E. US and E. China is 10-11%.
3. Enhancements are accompanied by Hydrophobic-to-Hydrophilic transformation related mainly to the enhanced condensation of gas phase H_2SO_4 and HNO_3 on aerosol particles.

- **Comparison with Measurements**

Summary of the comparison of the Base_S1 and S1 model simulations to observations of aerosol concentrations during January-March 2001. OAM and MAM are the arithmetic mean of the observations and of the model, respectively, in $\mu g\ m^{-3}$. MAM and OAM represent co-located measurements and model results (i.e., based on the locations of the observations).

species	network	Nr. of stations	OAM	MAM [$\mu g\ m^{-3}$]		MAM/OAM	
				base_S1	S1	base_S1	S1
SO_4^{2-}	CASTNET	53	3.17	2.57	3.05	0.81	0.96
	EMEP	80	2.00	2.95	3.09	1.48	1.55
	EANET	11	2.82	2.89	3.13	1.03	1.11
NO_3^-	CASTNET	53	1.27	1.81	1.97	1.43	1.55
	EMEP	27	1.75	2.24	2.42	1.28	1.38
	EANET	10	0.81	1.26	1.14	1.55	1.41
NH_4^+	CASTNET	53	1.26	1.23	1.43	0.98	1.14
	EMEP	21	1.00	1.43	1.54	1.43	1.54
	EANET	9	0.96	0.96	1.02	1.01	1.07

➢ General increase in the Mean modelled/observed ratio.
➢ Simulating realistic HONO levels Improve the sulphates modelled/observed ratios in eastern US.
➢ Nitrates modelled/observed ratios are improved in E. Asia.
➢ Ammonium are generally well simulated.

Conclusion

➢ Simulating Realistic HONO levels lead to:
1. Enhanced HO_x, H_2O_2, HNO_3, H_2SO_4 in high NO_x regions, especially in winter, when other photolytic sources are of minor importance.
2. Enhanced sulphate aerosol mainly due to enhanced oxidation of SO_2 with OH. Though H_2O_2 oxidation is the main source of sulphates, it did not contributed to enhanced SO_4^{2-} due to the S(IV) limited conditions in most regions except in E. Asia.
3. Enhanced Nitrates due to enhanced HNO_3, in ammonia-rich regions.
4. Enhanced aerosol number concentration accompanied with transformations from hydrophobic to hydrophilic. The enhancement of aerosol number and solubility implies potential impacts on the cloud nucleation properties and the particle liftime.

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